

## Supramolecular Chemistry

## Redox-Driven Transformation of a Discrete Molecular Cage into an Infinite 3D Coordination Polymer

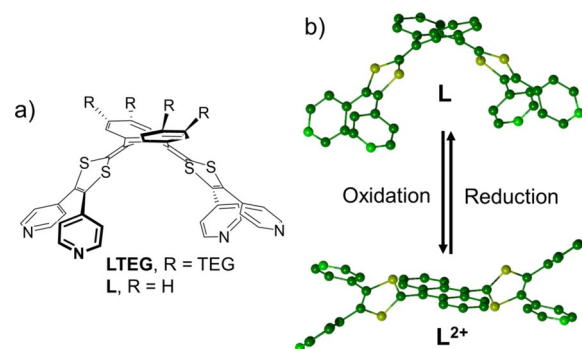
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**Abstract:** Two  $M_{12}L_6$  redox-active self-assembled cages constructed from an electron-rich ligand based on the extended tetrathiafulvalene framework (exTTF) and metal complexes with a linear geometry ( $Pd^{II}$  and  $Ag^I$ ) are depicted. Remarkably, based on a combination of specific structural and electronic features, the polycationic self-assembled  $Ag^I$  coordination cage undergoes a supramolecular transformation upon oxidation into a three-dimensional coordination polymer, that is characterized by X-ray crystallography. This redox-controlled change of the molecular organization results from the drastic conformational modifications accompanying oxidation of the exTTF moiety.

Reversible coordination bonds have been intensively employed for the preparation of both discrete and infinite supramolecular assemblies. In particular, coordination polymers have focused a strong attention for various types of application such as gas storage/ separation, catalysis, detection, and even for molecular analysis.<sup>[1]</sup> Beyond inducing polymerization, the coordination bond has also been extensively used to drive the construction of discrete bi- or three-dimensional self-assembled architectures in a single step and with quantitative yields.<sup>[2,3]</sup> The corresponding generated cavities make those systems eligible for various applications, for example in host-guest chemistry, catalysis, or drug delivery.<sup>[4]</sup> Importantly, the dynamic nature of the coordination bonds guiding those self-assembly processes allows them to undergo supramolecular transformations driven by external stimuli, irradiation, guest exchange, and solvent or metal substitution. These transforma-

tions may lead to new discrete structures differing by the shape or by the metal to ligand stoichiometry,<sup>[5]</sup> as well as to 1D supramolecular polymers.<sup>[6]</sup>

In the course of our studies related to electron-rich and redox-active coordination-driven self-assemblies,<sup>[7]</sup> we are particularly interested in using ligands based on the so called extended tetrathiafulvalene moiety (exTTF).<sup>[8]</sup> The latter is characterized by a high  $\pi$ -donating ability and is able to generate a dicationic species ( $exTTF^{2+}$ ) according to a two-electron oxidation. A key feature of this unit relies on its geometry, which is severely modified depending on the redox state. Whereas the neutral exTTF is highly curved because of intramolecular H...S interactions (Figure 1b), the corresponding oxidized species



**Figure 1.** a) Structure of exTTF-based tetrapyrrolyl ligands; b) X-ray structures of  $L^{[8d]}$  and  $L^{2+}$  (electrocrystallization,  $C = 6 \times 10^{-4}$  M,  $CH_2Cl_2$ ,  $nBu_4NPF_6$ , 0.5  $\mu A$ , 20 °C, 9 days).  $PF_6^-$  anions omitted for clarity.

$exTTF^{2+}$  exhibits a fully aromatic relaxed conformation with two 1,3-dithiolium rings linked to a central planar anthracene moiety.<sup>[9]</sup> This is illustrated by the X-ray diffraction (XRD) studies led on  $L^{[8d]}$  and on the hereafter characterized electro-crystallized  $L^{2+}$  salt (Figure 1b and Supporting Information). Taking advantage of this unique feature, we recently demonstrated that an exTTF-based  $M_4L_2^{8+}$  container can be reversibly disassembled through an electrochemical stimulus into the corresponding oxidized ligands and metal complexes.<sup>[8b]</sup> Nevertheless, to the best of our knowledge, there is no example yet, describing the transformation of a supramolecular discrete structure into an infinite three-dimensional architecture through an external redox stimulus.

We report herein the synthesis of two large redox-active  $M_{12}L_6$  neutral and polycationic self-assembled cages, respectively, constructed upon assembling between an extended tet-

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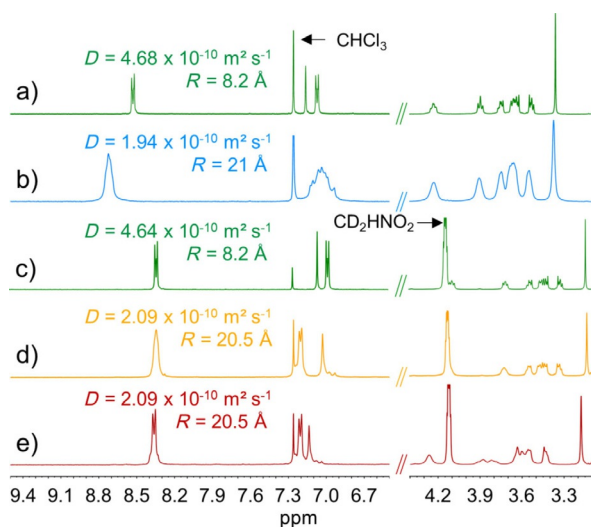
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rathiafulvalene ligand (**LTEG**) and two different metal complexes ( $\text{Pd}^{\text{II}}$  and  $\text{Ag}^{\text{I}}$  respectively) possessing a linear coordination geometry. We demonstrate that addition of an excess of silver cations onto the polycationic cage leads to the formation of an infinite three-dimensional supramolecular polymer, that could be characterized by XRD.

Ligand **LTEG**<sup>[8b]</sup> and *trans*  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (2 equiv.) were mixed in DMSO at 100 °C to afford a neutral self-assembled cage ( $\text{Pd}_{12}(\text{LTEG})_6$ ) (in which **Pd** corresponds to  $\text{PdCl}_2$ ). After precipitation with ethyl acetate, the resulting solid was characterized in  $\text{CDCl}_3$  by  $^1\text{H}$  NMR and  $^1\text{H}$  DOSY NMR spectroscopy (Figure 2). Compared to the starting ligand **LTEG** (Figure 2a),



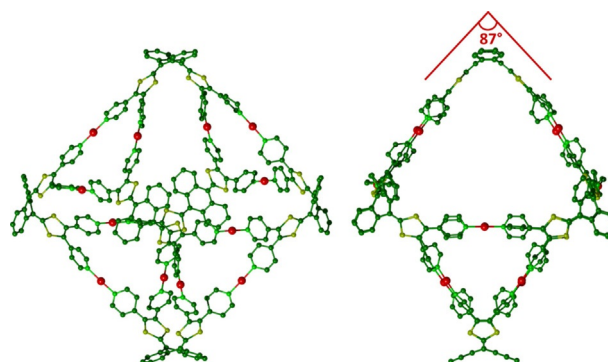
**Figure 2.**  $^1\text{H}$  NMR spectra and corresponding diffusion coefficients extracted from  $^1\text{H}$  DOSY NMR experiments a) ligand **LTEG** in  $\text{CDCl}_3$ , b) cage  $\text{Pd}_{12}(\text{LTEG})_6$  in  $\text{CDCl}_3$ , c) ligand **LTEG** in  $\text{CDCl}_3/\text{CD}_3\text{NO}_2$  (1/1), d) cage  $[\text{Ag}_{12}(\text{LTEG})_6]^{12+}$  in  $\text{CDCl}_3/\text{CD}_3\text{NO}_2$  (1/1) and e)  $[\text{Ag}_n(\text{Ag}_{12}\text{LTEG})_6]^{1(n+12)+}$  in  $\text{CDCl}_3/\text{CD}_3\text{NO}_2$  (1/1).

the quantitatively isolated species shows broader NMR signals than usual for large discrete structures (Figure 2b).<sup>[10]</sup> The formation of a single discrete compound is established by  $^1\text{H}$  DOSY, for which only one set of signals is observed, with a diffusion value of  $D = 1.93 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . A calculated Stokes radius<sup>[11]</sup> of 21 Å confirms the formation of a large size self-assembled structure. Performing ESI mass spectrometry of neutral metal complexes is usually challenging, in particular for high molecular weight compounds. We took advantage of the cation binding ability of the TEG chains to stabilize ionic species, to characterize the system by MS. The ESI-FTICR (Fourier-transform ion cyclotron resonance) experiments were therefore carried out in presence of  $\text{KOTf}$ , which allowed us to determine unambiguously a  $\text{M}_{12}\text{L}_6$  stoichiometry (i.e.,  $\text{Pd}_{12}(\text{LTEG})_6$ ) with characteristic peaks corresponding to the  $[\text{Pd}_{12}(\text{LTEG})_6 + (\text{KOTf})_{n=9-12-7\text{OTf}}]^{7+}$  and to the  $[\text{Pd}_{12}(\text{LTEG})_6 + (\text{KOTf})_{n=7-11-6\text{OTf}}]^{6+}$  cations (Figure S12).

Besides the above neutral  $\text{M}_{12}(\text{LTEG})_6$  supramolecular cage, a similar polycationic one was prepared from a silver cation. The reaction between **LTEG** and 2 equivalents of  $\text{AgBF}_4$  was fol-

lowed by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3/\text{CD}_3\text{NO}_2$  (1/1) (Figure 2d). This mixture produced instantaneously a single discrete structure presenting a diffusion coefficient of  $2.19 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ; a value which characterizes a cavity size similar to the one observed above for the palladium cage  $\text{Pd}_{12}(\text{LTEG})_6$ .<sup>[12]</sup> An  $\text{M}_{12}\text{L}_6$  stoichiometry, consistent with the latter observation, could be established by ESI-FTICR, with characteristic signals corresponding to the  $[\text{Ag}_{12}(\text{LTEG})_6]^{12+}$  cage (Figure S13 in Supporting Information). Note that a similar self-assembly experiment carried out in  $\text{CH}_3\text{CN}$ , did not afford any supramolecular discrete structure (Figures S14–S17), illustrating the crucial role of solvents in coordination driven self-assembly processes. In addition, it is worth noting that 2 equivalents of silver cations are sufficient to generate the self-assembly, in accordance with a metal coordination process involving solely the pyridyl units and not the TEG chains.

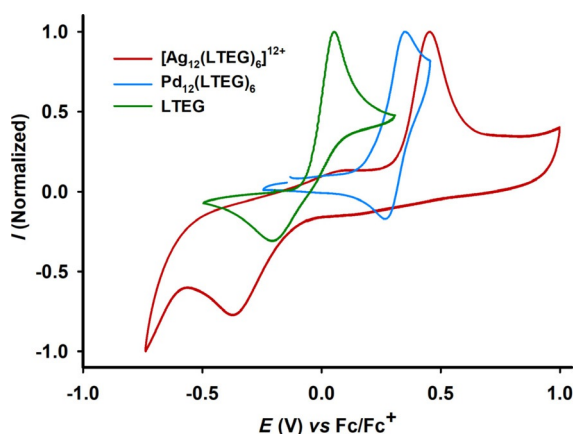
This behavior is corroborated by  $^1\text{H}$  NMR study, since no evolution of the TEG signals was observed along the self-assembly process (Figure 2c,d). Since no single crystal suitable for X-ray analysis could be grown from those  $\text{M}_{12}(\text{LTEG})_6$  structures, molecular force field (MM+) optimization studies were undertaken (Figure 3 and Figure S18 in Supporting Informa-



**Figure 3.** MM+ simulation of cage  $[\text{Ag}_{12}(\text{LTEG})_6]^{12+}$ .

tion). They consistently converge towards a square-based bipyramidal geometry in which the silver (or palladium) atoms adopt a nearly linear geometry ( $\text{Pyr}-\text{Ag}-\text{Pyr}$ : ca. 175°). In addition, the curvature of the ligands, characterized by the intramolecular angle between both 1,3-dithiol-2-ylidene mean planes, is of 87–89° (Figures 3, Figure S18), a value which is similar to the free ligand one (**L**: 86°, Figure 1b). Such values illustrate a good geometrical matching between both counterparts (ligand and metal complex) and the absence of conformational energy cost upon the self-assembly process. The resulting cavities are calculated to exhibit a very large volume of approximately 4200 Å<sup>3</sup> (Figures S19 and S20).<sup>[13]</sup>

The electrochemical properties of ligand **LTEG** and cages  $\text{Pd}_{12}(\text{LTEG})_6$  and  $[\text{Ag}_{12}(\text{LTEG})_6]^{12+}$  were studied by cyclic voltammetry (Figure 4). Due to solubility issues, distinctive solvents were used for the three compounds. As usually observed for exTTF derivatives, **LTEG** shows a pseudo-reversible wave involving two electrons at  $E_1^{\text{ox}} = +0.05 \text{ V}$  versus  $\text{Fc}/\text{Fc}^+$ . This oxidation wave is shifted to a higher potential at  $E_1^{\text{ox}} = +0.35 \text{ V}$

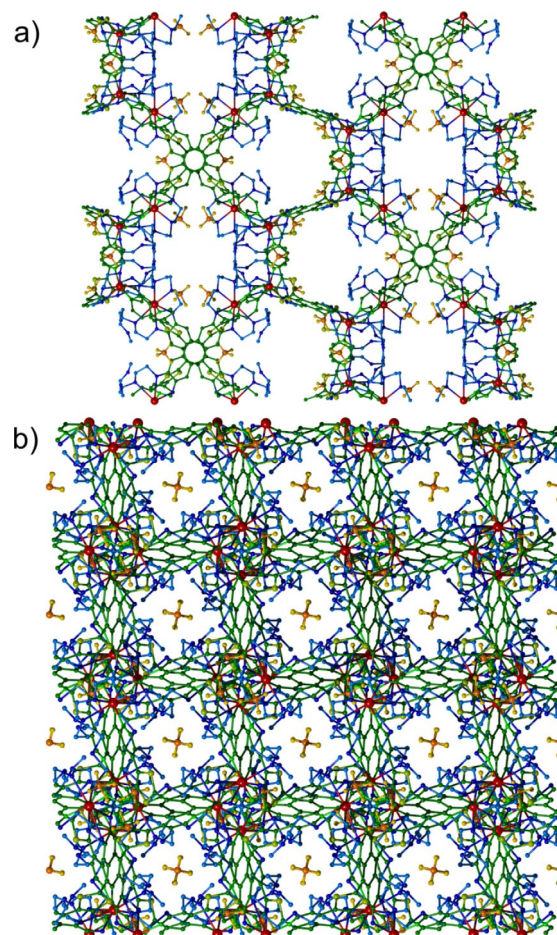


**Figure 4.** Normalized cyclic voltammogram of ligand **LTEG** ( $C = 10^{-3}$  M,  $\text{CH}_3\text{CN}$ ) and of cages **Pd<sub>12</sub>(LTEG)<sub>6</sub>** ( $C = 5 \times 10^{-4}$  M,  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  (1/1)) and **[Ag<sub>12</sub>(LTEG)<sub>6</sub>]<sup>12+</sup>** ( $C = 5 \times 10^{-4}$  M,  $\text{CH}_3\text{NO}_2/\text{CH}_2\text{Cl}_2$  (1/1)), 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>, 100 mV s<sup>-1</sup>, GC, V vs. Fc/Fc<sup>+</sup>.

versus Fc/Fc<sup>+</sup> in the case of cage **Pd<sub>12</sub>(LTEG)<sub>6</sub>**, as expected from coordination to the palladium center. It is worth noting that the process is quasi-reversible in this case, suggesting that the integrity of the cage is preserved upon oxidation. Consistently, we recently reported a similar (reversibility and  $E_{ox}$ ) behavior for a neutral **Pt<sub>4</sub>(LTEG)<sub>2</sub>** self-assembly (see Figure S21 for comparison).<sup>[8a]</sup> On the other hand, a strikingly different behavior is observed for the polycationic cage **[Ag<sub>12</sub>(LTEG)<sub>6</sub>]<sup>12+</sup>**. Again, the oxidation wave is located at a higher potential of  $E_{1^{ox}} = +0.45$  V versus Fc/Fc<sup>+</sup> in comparison with ligand **LTEG**, but in this case the corresponding reduction process occurs at a very low value ( $E_{1^{red}} = -0.36$  V). The latter appears very close to the one already observed for another polycationic exTTF based self-assembly (**Pd<sub>4</sub>(LTEG)<sub>2</sub>**)<sup>8+</sup>, for which we unambiguously demonstrated the cage disassembling upon oxidation (see Figure S22 for comparison).<sup>[8b]</sup>

On this basis, we were interested in further testing the behavior of the polycationic **[Ag<sub>12</sub>(LTEG)<sub>6</sub>]<sup>12+</sup>** upon chemical oxidation, and in identifying the products following the cage disassembly process. The latter process was monitored by <sup>1</sup>H NMR spectroscopy. Upon addition of 12 equivalents of AgBF<sub>4</sub> to the **[Ag<sub>12</sub>(LTEG)<sub>6</sub>]<sup>12+</sup>** complex, the anthracenyl protons signals were only slightly downfield-shifted, whereas a significant modification of the TEG signals was observed, and the diffusion coefficient value (*D*) remained constant (Figure 2e, Figures S23–S24). This result suggests that silver cations, which are introduced in excess, are complexed by the peripheral TEG chains to form a **[Ag<sub>n</sub>(Ag<sub>12</sub>LTEG)<sub>6</sub>]<sup>(n+12)+</sup>** species. Therefore, contrary to previous observations which showed that Ag<sup>+</sup> allows oxidation of exTTF derivatives,<sup>[8a]</sup> no oxidation of the system can be observed in the present case in this medium, presumably because of the binding of Ag<sup>+</sup> cations by the lateral TEG chains. One can note that addition of a supplementary excess of AgBF<sub>4</sub> (up to 30 equiv.) did not affect the <sup>1</sup>H NMR spectrum either (Figure S25). Nevertheless, while cage **[Ag<sub>12</sub>(LTEG)<sub>6</sub>]<sup>12+</sup>** is stable in a CD<sub>3</sub>NO<sub>2</sub>/CDCl<sub>3</sub> solution for weeks, a slight gray suspension appears and the subsequent formation of light greenish insoluble monocystals that could

be easily isolated in 66% yield by filtration, was observed after one week in the same solvent mixture. An X-ray diffraction analysis of the latter reveals that the initial self-assembled cage structure **[Ag<sub>12</sub>(LTEG)<sub>6</sub>]<sup>12+</sup>** undergoes a structural evolution following a self-oxidation process, into an infinite three-dimensional supramolecular polymer **[(Ag<sub>2</sub>LTEG<sub>ox</sub>)<sup>4+</sup>]<sub>x</sub>** (Figure 5), for

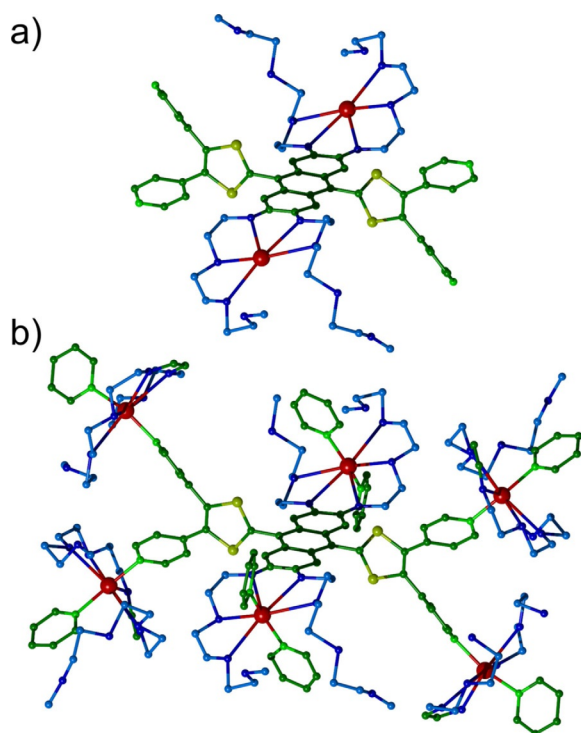


**Figure 5.** X-ray structure of the three-dimensional supramolecular polymer **[(Ag<sub>2</sub>LTEG<sub>ox</sub>)<sup>4+</sup>]<sub>x</sub>**; BF<sub>4</sub><sup>-</sup> anions are located in the free space; view along the *a* axis (a); along the *c* axis (b).

which all the exTTF units have been oxidized into the dicationic state (**LTEG<sub>ox</sub>**). This process is supposed to occur through a kinetically delayed oxidation process promoted by the silver cations bound to the TEG units and, to the best of our knowledge, corresponds to a unique example of a supramolecular transformation between a discrete cage and a 3D-polymer. Finally, addition of reducing agent tetrakis(dimethylamino)ethylene (TDAE) to a suspension of **[(Ag<sub>2</sub>LTEG<sub>ox</sub>)<sup>4+</sup>]<sub>x</sub>** in a CD<sub>3</sub>NO<sub>2</sub>/CDCl<sub>3</sub> mixture, leads to the instantaneous formation of the neutral ligand **LTEG**, without reformation of the initial cage.

The polycationic polymeric backbone **[(Ag<sub>2</sub>LTEG<sub>ox</sub>)<sup>4+</sup>]<sub>x</sub>** is constituted from the repeating (**Ag<sub>2</sub>LTEG<sub>ox</sub>**)<sup>4+</sup> unit (Figure 6a), in which the ligand is oxidized to its dicationic state (**LTEG<sub>ox</sub>**), with typical C–C bond lengths of 1.47 Å between 1,3-dithiolium rings and the planar central anthracene moiety, and with





**Figure 6.** Partial  $[(\text{Ag}_2\text{LTEG}_{\text{ox}})^{4+}]_x$  X-ray structure showing a) the repeating  $(\text{Ag}_2\text{LTEG}_{\text{ox}})^{4+}$  motifs and b) the silver coordination sphere.  $\text{BF}_4^-$  anions omitted for clarity.

corresponding dihedral angles of  $83.4^\circ$ . The TEG chains display a key role in structuring the polymer, since they contribute, in addition to two pyridine units ( $\text{N}-\text{Ag}-\text{N}=157^\circ$ ), to coordinate silver cations (Figure 6b). Consequently, three independent exTTF ligands are simultaneously involved in the silver coordination. One can note that a coordination polymer constructed from a tetrathiafulvalene ligand bearing a crown ether moiety has already been described, but the latter binding site was not involved in the polymeric construction.<sup>[14]</sup>

In summary, we report herein the preparation of two electro-active  $\text{M}_{12}\text{L}_6$  cages constructed from an electron-rich exTTF ligand and associating palladium or silver complexes with a linear coordination geometry. The resulting cavities display very large volumes of about  $4000 \text{ \AA}^3$ . Thanks to the unique feature of the exTTF unit to drastically change its geometry through a redox stimulus, we demonstrate that a discrete cage  $[\text{Ag}_{12}(\text{LTEG}_{\text{ox}})_6]^{12+}$  can evolve into a polycationic three-dimensional supramolecular polymer  $[(\text{Ag}_2\text{LTEG}_{\text{ox}})^{4+}]_x$  upon oxidation, and that the latter is induced by silver cations coordinated in the TEG chains. To the best of our knowledge, this supramolecular transformation constitutes a first example of a structural evolution from a discrete coordination cage to a three-dimensional supramolecular polymer; two major classes of supramolecular coordination compounds. In addition, even though several examples of coordination polymers based on the parent tetrathiafulvalene unit are described,<sup>[15]</sup>  $[(\text{Ag}_2\text{LTEG}_{\text{ox}})^{4+}]_x$  constitutes the first example of a three-dimensional coordination network involving an exTTF derivative.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** coordination cages • coordination polymers • extended tetrathiafulvalenes • redox • self-assembly

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- [12] A hydrodynamic radius of 20.5 Å could be calculated from a DOSY experiment carried out in pure CD<sub>3</sub>NO<sub>2</sub> (Figure S11).
- [13] a) The cavity volume has been estimated based on Voidoo algorithm using ABSiCC (Automating Boring Stuff in Computational Chemistry), a home-made POV-Ray-interfaced program designed by Thomas Cauchy and written by Yohann Morille, Angers University; b) The model provides a value of 35.6 Å for the size of the rigid part of the cage (i.e., without taking into account the flexible lateral TEG chains). This value is therefore consistent with the 42 Å value determined by DOSY NMR.
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